Eurasian Journal of Physics and Functional Materials

Volume 8 | Number 4

Article 5

Pages: 1 - 7

2024

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Recommended Citation
Davletshina, Alisa D.; Yakshibaev, Robert A.; Balapanov, Malik Kh.; and Kubenova, Marzhan M. (2024) "The band structure of semiconducting tetragonal Na4Cu2S3 phase," *Eurasian Journal of Physics and Functional Materials*: Vol. 8: No. 4, Article 5.
DOI: https://doi.org/10.69912/2616-8537.1236

ORIGINAL STUDY

The Band Structure of Semiconducting Tetragonal $Na_4Cu_2S_3$ Phase

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Abstract

Previously unknown the band structure of $Na_4Cu_2S_3$ compound has been calculated from first principles. According to the obtained results, the compound exhibits semiconducting properties. The $Na_4Cu_2S_3$ compound has the band gap 2.164 eV and it is characterized by a high density of states near the Fermi level.

Keywords: Band structure, Chalcogenides, Semiconducting material, Copper sulfide

1. Introduction

Copper chalcogenides exhibit high ionic conductivity along with predominant electronic conductivity [1—4]. The ionic conductivity in the studied compounds is provided by copper cations and is ~1—3 $Ohm^{-1}cm^{-1}$, which is comparable to the ionic conductivity in liquid electrolyte solutions. In terms of electronic properties, binary copper chalcogenides are p-type semiconductors and the conductivity strongly depends on the degree of non-stoichiometry on the cationic sublattice. The interest in studies of chalcogenide systems is mainly due to the fact that they exhibit highest thermoelectric properties and are used in autonomous current sources [5,6].

Attempts to improve the thermoelectric efficiency of binary chalcogenides by changing the composition along the chalcogenide sublattice (X = S, Se, Te) or metal sublattice (M = Cu, Ag) did not lead to significant progress. Therefore, attempts have been made to alloy copper sulfides with alkali metals (Li, K, Na) in order to obtain higher values of thermoelectric efficiency.

In this regard, $Cu_{2-x}Na_xS$ systems are promising, in which a number of stable phases or chemical compounds appear depending on the alkali metal content. For example, the semiconducting $Na_2Cu_4S_3$ phase has a monoclinic lattice, space group C2/m (12). It is known that $Na_2Cu_4S_3$ crystallites have a chain structure and strong anisotropy [7]. At room temperature, for pressed samples, the conductivity of $Na_2Cu_4S_3$ is about 300 Om^{-1} cm^{-1}. The $Na_{0.05}Cu_{1.95}S$ compound described in work [8] showed the highest Seebeck coefficient 1.2 mV/K at 650 K. The highest dimensionless thermoelectric figure of merit ZT = 1.1 was obtained at 773 K for $Na_{0.01}Cu_{1.8}S$ in work [9]. For the $Na_{0.4}Cu_{1.55}S$ sample, a high value of ZT = 0.84 was observed at 630 K [10].

Thermoelectric efficiency ZT depends on temperature and it is determined by a combination of parameters:

$$zT = \frac{\sigma S^2 T}{\kappa},$$

where σ - electrical conductivity, κ - thermal conductivity, S - Seebeck coefficient.

To obtain materials with high value of thermoelectric efficiency, it is necessary to know the features of the band structure, which determines the electrophysical properties of materials.

A significant number of studies [11—20] are devoted to the study of the band structure and electronic properties of binary Cu_2S and Na_2S sulfides. Calculations of the copper sulfide band structure for various non-stoichiometric compositions and crystal structures have been carried out in Refs. [11—17], according to which the band gap values range from 0 to 0.313 eV. In one of the early experimental works [18], the values of

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Received 8 November 2024; revised 25 November 2024; accepted 29 November 2024.

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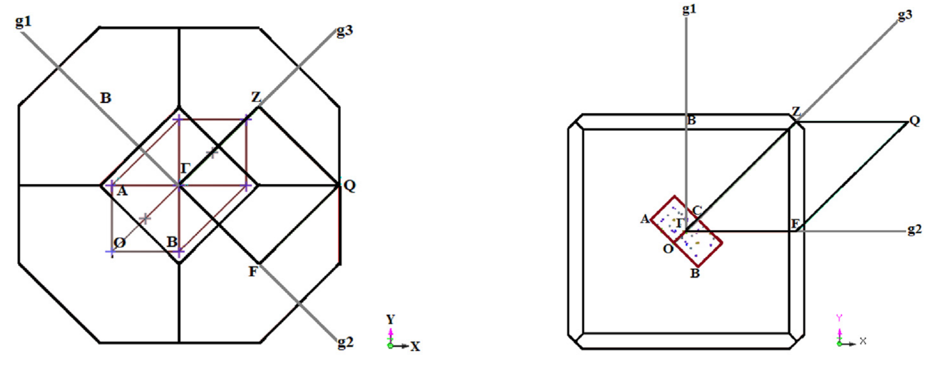
https://doi.org/10.69912/2616-8537.1236

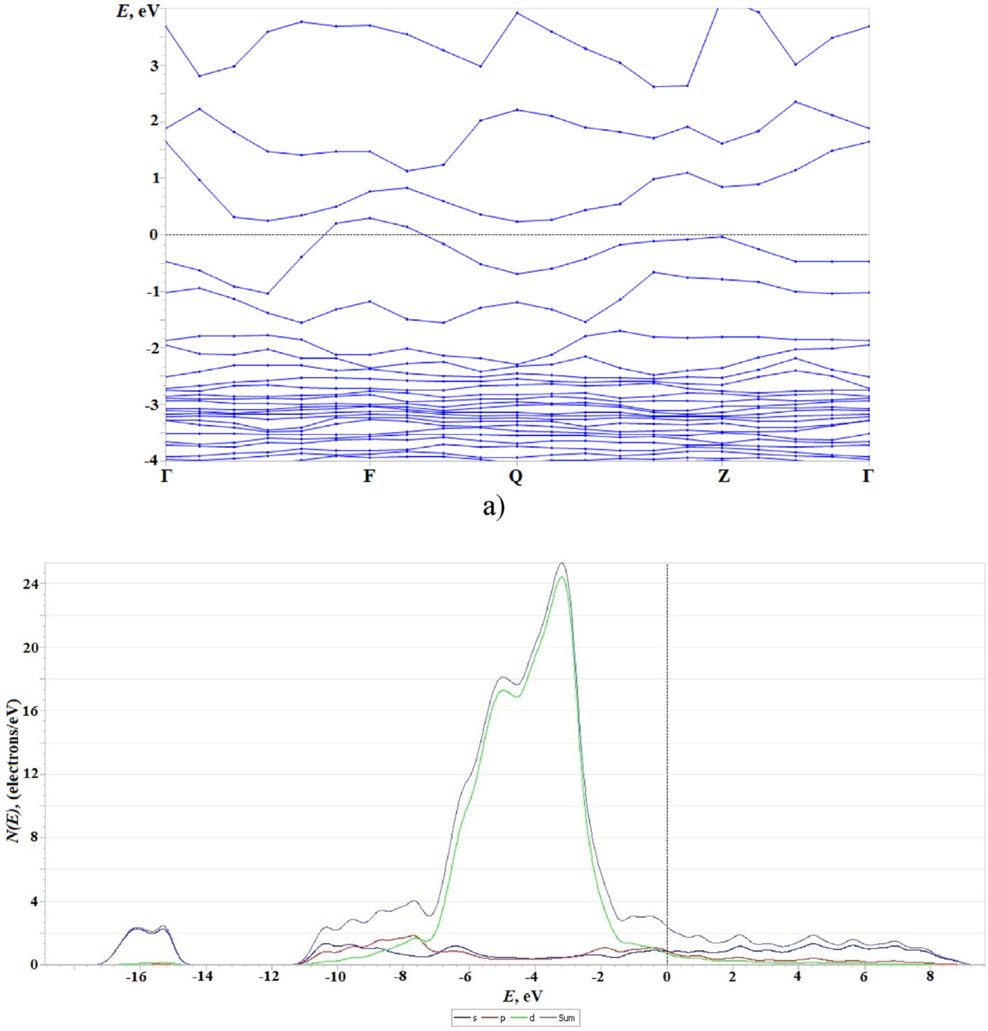


a) b)

Fig. 1. The 1st Brillouin zone of FCC (a) and tetragonal (b) structure.

the band gap widths of 1.4 and 1.3 eV were obtained for Cu_2S in the solid and liquid phases, respectively. Sodium sulfide is a semiconductor with a band gap of 0.96–2.566 eV depending on the Na content [19,20]. In Ref. [21], the calculation of the of $NaCu_5S_3$ band structure to assess the spin splitting was performed. The band structure of $Na_4Cu_2S_3$ is unknown now, and its thermoelectric properties have not been studied.

A review of the literature data on the band structure shows that there is no quantitative agreement between



a)

b)

Fig. 2. The band structure (a) and density of states (b) of Cu_2S in the tetragonal phase.

the calculated values of the band gap and the experimental ones for copper sulfide, and there are no experimental studies for sodium sulfide.

In this work, the band structure of $Na_4Cu_2S_3$ compound was calculated using the BIOVIA Materials Studio DMol^3 program [22], which allowed us to study its electronic structure with a sufficiently large range of exchange-correlation functionals.

2. Calculation method

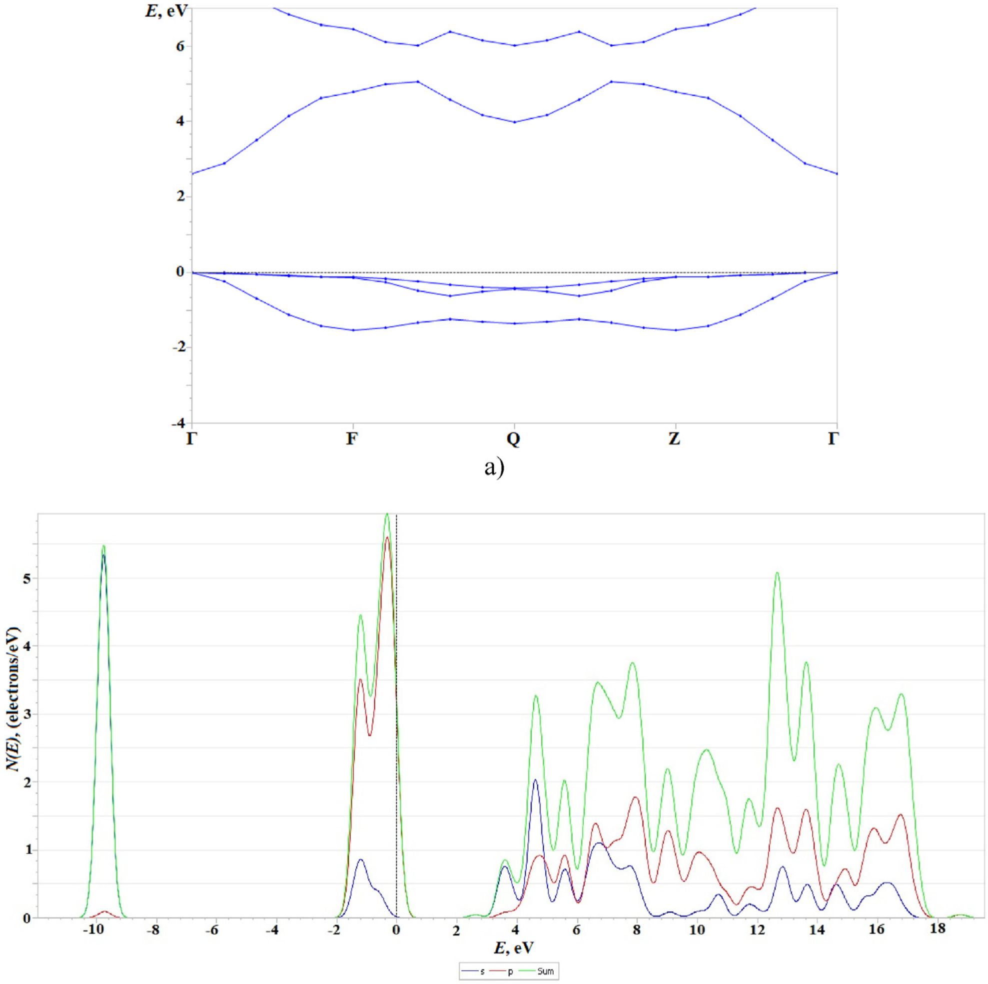
The calculations of the band structure of the studied compounds were performed using the BIOVIA Materials Studio $DMol_3$ program, which is based on the electron density functional theory [22]. During the calculations, exchange-correlation effects were taken into account in the general-gradient-approximation (GGA). The accuracy of self-consistent SCF tolerance calculations is of the order of 10^{-5}. The values of the reciprocal lattice k-points are specified using the Monkhorst—Pack method [23] on a 2 × 2 × 2 grid.

Band structure calculations were done with a = 6.57 Å, b = 3.93 Å for the tetragonal Cu_2S phase [24], and with a lattice parameter a = 6.53 Å for the cubic Na_2S phase [24] in order to test the calculation method and for $Na_4Cu_2S_3$ tetragonal phase with parameters a = 9.52 Å, b = 36.55 Å [24—26]. The calculation was performed relative to points Γ (0 0 0), F (0 0.5 0), Q (0 0.5 0.5), Z (0 0 0.5), B (0.5 0 0) of the 1st Brillouin zone (Fig. 1), i.e. not strictly tied to the symmetry of the structure.

3. Results and discussion

Fig. 2 shows the band structure of the tetragonal Cu_2S phase. Copper sulfide in the tetragonal phase is a degenerate semiconductor. The top of the valence band is formed predominantly by p-levels of sulfur and d-levels of copper, and the bottom of the conduction band is formed by p-levels of sulfur and s-levels of copper. The largest contribution to conductivity is made by p-electrons of sulfur and d-electrons of copper. These results are in satisfactory agreement with the data of the work [27].

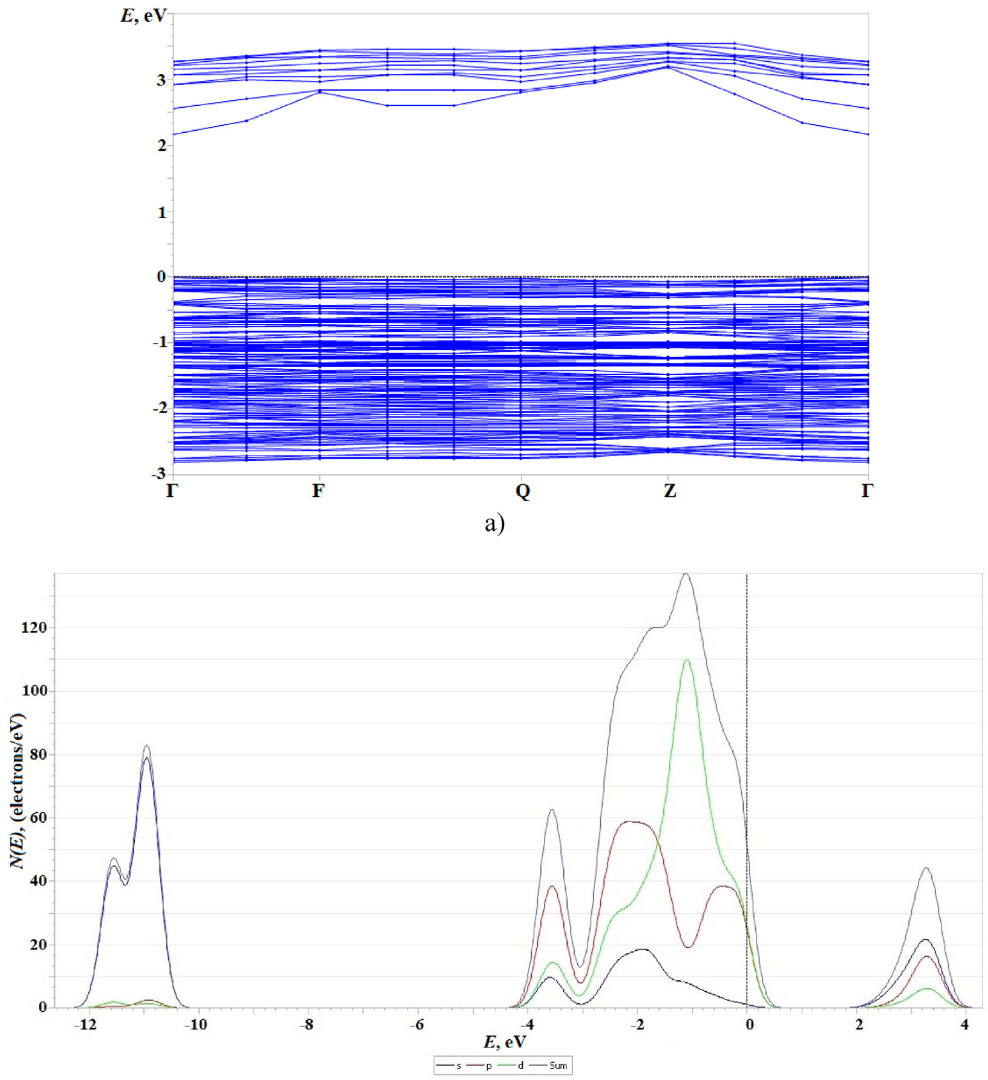
In the case of Na_2S, the band gap is 2.608 eV (Fig. 3a), which is in good agreement with literature



a)

b)

Fig. 3. The band structure (a) and density of states (b) of Na_2S in the cubic phase.



a)

b)

Fig. 4. The band structure (a) and density of states (b) of $Na_4Cu_2S_3$ in the tetragonal phase.

data [19]. The valence band is formed by the s-states of Na and the p-states of S, and the conduction band by the s-, p-states of S and the s-states of Na with equal contributions.

Further, we calculated the band structure of $Na_4Cu_2S_3$, which is presented in Fig. 4. The band gap for this compound is 2.164 eV. Analysis of the density of states (Fig. 4, b) shows that the top of the valence band is formed predominantly by p-states of sulfur and d-states of copper, the contribution of s-states of sodium is insignificant, and the bottom of the conduction band is formed by s-states of copper and sodium and p-states sulfur, the contribution of which to this band is almost the same. The increase in copper content increases the density of electronic states near the top of the valence band.

$Na_4Cu_2S_3$ has a fairly large band gap due to the high Na content and to the type of crystal lattice, which is a superlattice with a triple unit cell parameter.

4. Conclusion

An analysis of the results obtained from calculating the band structure showed that the $Na_4Cu_2S_3$ compound should exhibit semiconductor properties. The $Na_4Cu_2S_3$ compound has a band gap is 2.164 eV and it is characterized by a high density of states near the Fermi level. High density of states near the Fermi level can contribute to high sensitivity of electrical properties to external influences, since in kinetic effects the state of electrons near the Fermi level changes first. It will be interesting to further study the electrical properties of the compound, including thermoelectric ones.

Conflict of interest

Authors have not conflict of interests.

Funding and acknowledgments

The research was supported by the Ministry of Science and Higher Education of Kazakhstan (project No. AP23490700).

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